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Syntheses and Reactions of Iron(II) Complexes Containing Diphosphine Ligands with Pendant Nitrogen Bases

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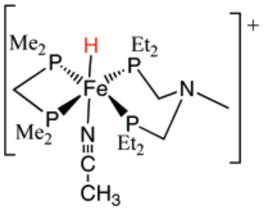
A series of new iron(II)−hydride complexes that contain diphosphine ligands with pendant amine bases of the formula *cis*-$[HFeL(PNP)_2]^+$, where PNP = $Et_2PCH_2NMeCH_2PEt_2$ and L = CH_3CN (**3**), CO (**4**), $P(OEt)_3$ (**5**), have been synthesized and characterized. Protonations of the pendant bases in the PNP complexes have been characterized, and for selected complexes, pK_a values have been determined. The acidity of the PNHP ligand depends significantly on the electronic properties of the Fe center to which it is bound, ranging from <7.0 to 12.7, depending on the nature of the coligands present. Unlike the previously studied hydride complexes $[HNi(PNP)_2]^+$ and *trans*-$[HFe(CH_3CN)(PNP)(dmpm)]^+$ (where dmpm is bis(dimethylphosphino)methane), the new hydride complexes reported here do not show rapid intramolecular exchange between the protonated base of the diphosphine and the hydride ligand. This is attributed to steric interactions between ethyl substituents on the PNP ligands.

Introduction

Many examples of metal complexes containing ligands with a noncoordinated, pendant amine base have been synthesized, and several of these have been studied to characterize features of intramolecular metal−hydride/N−H exchange and in attempts to promote heterolytic H−H or R−H activations.[1−8] We have been investigating the chemistry of first-row metal complexes containing diphosphine ligands that incorporate a pendant base in order to determine the role of the base as a proton relay and participant in hydrogen activation.[9−13] Complexes of the formula $[Ni(PNP)_2]^{2+}$, which contain an η^2-diphosphine ligand with a noncoordinated pendant amine, were found to react readily with hydrogen to form the heterolytic cleavage product $[HNi(PNHP)(PNP)]^{2+}$.[9] These complexes undergo rapid intramolecular proton/hydride exchange ($k \approx 10^4$ s^{-1} at room temperature) as well as intermolecular exchange with protons in solution.

Iron complexes containing the PNP ligand have also been synthesized and characterized.[10,12] We have shown previously that octahedral iron(II) complexes containing two chelating PNP ligands and two monodentate ligands adopt a cis geometry, as in *cis*-$[Fe(CH_3CN)_2(PNP)_2]^{2+}$, while those containing one PNP and a diphosphine ligand with a small chelate bite such as bis(dimethylphosphino)methane (dmpm) favor trans structures.[10] The pendant base in the PNP ligand of *trans*-$[HFe(PNP)(dmpm)(CH_3CN)]BF_4$ (**1**) was found to promote very rapid intra- and intermolecular proton−hydride exchange in the Fe(II) complex.[12] For example, the endo isomer of the N-protonated hydride complex $[HFe(PNHP)(dmpm)(CH_3CN)]^{2+}$ (**1-H**) undergoes intramolecular proton−hydride exchange with a rate constant of 7.3 s^{-1} at −60 °C, corresponding to an exchange rate of approximately 2 × 10^4 s^{-1} at room temperature. In contrast, no intramolecular exchange was observed for the exo isomer of this N-protonated hydride complex. NMR studies also established that intermolecular proton exchange of the N−H proton of **1-H** with a weak external acid proceeds at rates even faster than the intramolecular exchange process.



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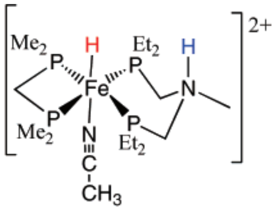

1-H

In this paper we report the synthesis and characterization of additional octahedral Fe(II) complexes containing two PNP

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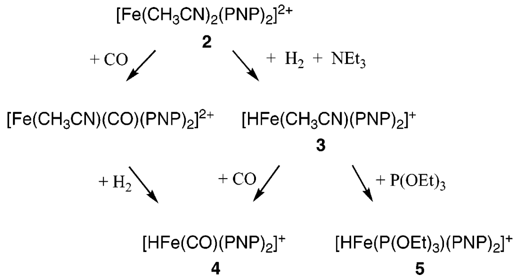
Scheme 1



chelates of the formula *cis*-$[HFe(PNP)_2L]^+$, where L = CH_3CN, CO, $P(OEt)_3$. A study of the intermolecular and intramolecular proton−hydride exchange properties mediated by the nitrogen base in the PNP ligand reveals significant differences from those characterized for the *trans*-$[HFe(PNP)(dmpm)L]^+$ derivatives studied previously. These fundamental studies of factors that influence the proton relay properties of pendant bases may be important in the development of synthetic catalysts[11,13] and may contribute to our understanding of mechanistic aspects of the iron-only hydrogenase enzymes.[14−16]

Results and Discussion

Syntheses and Characterizations of Iron Complexes with PNP Ligands. The syntheses of *cis*-$[Fe(PNP)_2XY]^{n+}$ derivatives is summarized in Scheme 1. The reaction of the previously reported[10] complex *cis*-$[Fe(PNP)_2(CH_3CN)_2](BF_4)_2$ (**2**) with hydrogen (1 atm) at room temperature in the presence of the external base triethylamine and the salt $NaBPh_4$ in acetone resulted in the formation of the hydride complex $[HFe(PNP)_2(CH_3CN)]BPh_4$ (**3**), which was isolated as a yellow crystalline solid. Complex **3** can also be synthesized by the addition of bis(triphenylphosphine)iminium borohydride to *cis*-$[Fe(PNP)_2(CH_3CN)_2](BF_4)_2$, but this method tends to give lower yields of pure product. The ^1H NMR spectrum of **3** reveals a hydride resonance at −11.11 ppm with a splitting pattern that corresponds to a doublet of doublet of triplets, and the $^{31}P\{^1H\}$ NMR spectrum of **3** shows an AMXZ spin system with 4 8-line multiplets (each a ddd). The data are consistent with a complex of C_1 symmetry with the two chelating PNP ligands in the cis geometry. A detailed listing of coupling constants and chemical shifts for these first-order NMR spectra are included in the Experimental Section. The infrared spectrum of this product shows absorptions for the iron−hydride stretch at 1824 cm^{-1} and for the C≡N stretch of the coordinated acetonitrile ligand at 2251 cm^{-1}.

An acetone solution of *cis*-$[HFe(PNP)_2(CH_3CN)]BPh_4$ (**3**) was purged with carbon monoxide and stirred for 20 h to form the pale yellow product *cis*-$[HFe(PNP)_2(CO)]BPh_4$ (**4**). The chemical shifts and coupling patterns in the ^{31}P and ^1H NMR data for **4** are similar to those of **3**, with the hydride multiplet occurring at −12.68 ppm. The infrared spectrum of **4** shows a strong CO stretch at 1931 cm^{-1} and a weak Fe−H stretch at 1898 cm^{-1}. Complex **4** can also be prepared by stirring an acetone solution of the previously reported[10] complex *cis*-$[Fe(PNP)_2(CH_3CN)(CO)][BPh_4]_2$ under an atmosphere of hydrogen, but this reaction is very slow and requires several days to proceed. Addition of an external base, such as NEt_3, to this reaction in order to promote heterolytic hydrogen cleavage leads to partial decomposition of the starting iron complex.

Complex **3** also reacts with triethyl phosphite in acetone to form *cis*-$[HFe(PNP)_2(P(OEt)_3)]BPh_4$ (**5**), which was isolated as a yellow solid. In the ^{31}P NMR spectrum of **5**, in addition to the four multiplets observed for the cis PNP ligands, a fifth resonance is observed at 166.7 ppm and assigned to the phosphite ligand. The phosphorus resonances are rather broad at room temperature, and all of the coupling patterns have not been resolved. The broadness does not appear to be due to phosphite ligand exchange. The ^{31}P NMR spectrum of a mixture of **5** and excess phosphite shows no evidence for exchange between free and coordinated phosphite at room temperature. In the ^1H NMR spectrum the multiplet of the hydride resonance (ddddd) is consistent with coupling to five inequivalent phosphorus nuclei. Coupling constants are given in the Experimental Section. Mass spectral data and elemental analyses also support the formulations of the new products **3**−**5**.

Ligand Exchange Reactions. Low-spin octahedral Fe(II) complexes are generally kinetically inert in ligand exchange reactions, but the rates of exchange of the coordinated acetonitrile ligands are relatively fast for the series of *cis*-$[Fe(PNP)_2(CH_3CN)L]^{n+}$ complexes. The disappearance of the coordinated acetonitrile resonance in the NMR spectrum of each complex was monitored using a 10-fold excess of CD_3CN in acetone-d_6. The exchange rate was independent of the acetontrile-d_3 concentration in acetone for *cis*-$[Fe(PNP)_2(CH_3CN)(CO)]^{2+}$, and a dissociative exchange mechanism is proposed for this and the other iron complexes. The half-lives for acetonitrile exchange of the cis bis(acetonitrile), hydride−acetonitrile, and carbonyl−acetonitrile derivatives were determined from the first-order kinetic plots (Figure S1; Supporting Information), and values of ca. 1, 6, and 34 min, respectively, were obtained at 23 °C in acetone.

The half-lives of acetonitrile exchange for the related trans derivatives $[Fe(CH_3CN)_2(PNP)(dmpm)]^{2+}$ and $[HFe(CH_3CN)(PNP)(dmpm)]^+$ were determined previously in CD_3CN at 23 ± 2 °C and were found to be 7.2 and 9.6 h, respectively.[10] The high lability of the cis derivatives relative to that of the trans complexes appears to be influenced both by the strong labilizing effect of a phosphine donor trans to the acetontirile ligand and also by steric interactions. The crystal structure of *cis*-$[Fe(CH_3CN)(CO)(PNP)_2]^{2+}$ has shown that the Fe−N bond distance for the nitrile ligand of 1.990(5) Å is 0.07 Å longer than that observed in the trans structure $[HFe(CH_3CN)(PNP)(dmpm)]^+$.[10] An ethyl substituent of one of the cis PNP ligands is in an orientation that eclipses the acetonitrile ligand, and this unfavorable steric interaction may contribute to the rate of acetonitrile dissociation.

Protonation of PNP Complexes and Determination of pK_a Values. Protonation reactions of selected cis-PNP complexes in acetonitrile solutions have been studied at room temperature in order to determine pK_a values for the protonated pendant amine base. The data permit an evaluation of potential proton relay properties of the ligand in these complexes and also allow a comparison with the previously reported pK_a values for the protonated PNP ligand in other complexes.[9,10]

Studies of the reaction of *cis*-$[Fe(PNP)_2(CH_3CN)_2](BF_4)_2$ (**2**; ^{31}P δ 22.0 and 14.5 ppm) with a series of acids have allowed us to identify both the mono- and diprotonated complexes. Reaction with a 5-fold excess of a strong acid such as triflic or tetrafluoroboric acid leads to the observation of new resonances

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in the ^{31}P NMR spectrum at limiting shifts of 29.9 and 20.7 ppm. These are assigned to the diprotonated complex *cis*-[Fe(PNHP)$_2$(CH$_3$CN)$_2$]$^{4+}$ (**2-2H**). Upon the addition of excess triethylamine, the ^{31}P chemical shifts of the original complex are observed. The diprotonated complex has been isolated as the BF$_4$ salt and further characterized. The N−H stretch is observed in the infrared spectrum at 2635 cm^{-1}, in the region expected for a tertiary ammonium ion.[17] In the ^{1}H NMR spectrum a singlet at 7.6 ppm is assigned to the NH protons, and when DOTf is used in the protonation reaction, a ^{2}H NMR resonance is observed at 8.3 ppm. Elemental analyses are also consistent with the diprotonated formulation.

The reactions of [Fe(PNP)$_2$(CH$_3$CN)$_2$](BF$_4$)$_2$ with weaker acids, tetrafluoroborate salts of *p*-cyanoanilinium (pK_a = 7.0 in CH$_3$CN)[18] and 2,4-dichloroanilinium, (p$K_a \approx 8$ in CH$_3$CN)[19] each resulted in the formation of a product with ^{31}P NMR shifts at 27.6 and 18.7 ppm. The same chemical shifts observed for the two different acids suggest that the monoprotonated complex *cis*-[Fe(PNP)(PNHP)(CH$_3$CN)$_2$]$^{3+}$ (**2-H**) is formed in each case. When the complex was reacted with varying ratios of 4-bromoanilinium/bromoaniline (pK_a = 9.43)[20] and monitored by ^{31}P NMR, chemical shifts intermediate between those of the nonprotonated and monoprotonated complexes were observed, and these were used to determine an equilibrium constant for the deprotonation of a single PNP ligand. The value of *K* was found to be [7.6(±0.1)] × 10^{-2}, and the pK_a value for **2-H** was calculated to be 8.3 ± 0.2 in acetonitrile at a temperature of 23 ± 2 °C. A similar procedure was used to determine a pK_a value of 9.2 ± 0.3 for the monoprotonated complex *cis*-[Fe(CO)(H)(PNHP)(PNP)]$^{2+}$.

Attempts to determine the pK_a of the monoprotonated derivative of **3**, e.g., *cis*-[HFe(CH$_3$CN)(PNHP)(PNP)]$^+$, were unsuccessful because the reaction of **3** with acids in acetonitrile at room temperature results in the rapid release of hydrogen (within ca. 1 min) and the formation of *cis*-[Fe(PNP)$_2$(CH$_3$CN)$_2$]$^{2+}$ or its protonated form. Rapid hydrogen evolution occurred, even with the weak acid anisidinium tetrafluoroborate (3 equiv, pK_a = 11.86 in CH$_3$CN).[20] This process is significantly slower for the previously studied trans complex *trans*-[HFe(CH$_3$CN)(dmpm)PNP)]$^+$ (**1**). In comparison, protonation of **1** with anisidinium ion at room temperature results in slow hydrogen loss over a period of a few hours, and equilibrium measurements at shorter time periods gave a pK_a value of 12.7.[10,21]

Table 1. pK_a Values in Acetonitrile for the PNHP Ligand in Iron and Nickel Complexes

complex	pK_a
cis-[Fe(PNP)(PNHP)(CH$_3$CN)(CO)]$^{3+}$	<7.0
cis-[Fe(PNP)(PNHP)(CH$_3$CN)$_2$]$^{3+}$ (**2-H**)	8.3
[Ni(dmpm)(PNHP)]$^{3+}$	8.7
cis-[Fe(PNP)(PNHP)(CO)(H)]$^{2+}$ (**4-H**)	9.2
cis-[Fe(PNP)(PNHP)(CH$_3$CN)(H)]$^{2+}$ (**3-H**)	fast H$_2$ release
trans-[Fe(PNHP)(dmpm)(CH$_3$CN)$_2$]$^{3+}$	9.4
trans-[Fe(PNHP)(dmpm)(CO)(H)]$^{2+}$	10.5
trans-[Fe(PNHP)(dmpm)(CH$_3$CN)(H)]$^{2+}$ (**1-H**)	12.7, slow H$_2$ release

The pK_a values for the protonated PNP ligand in a series of metal complexes are summarized in Table 1. The carbonyl complex *cis*-[Fe(PNP)(PNHP)(CH$_3$CN)(CO)]$^{3+}$ is the most acidic complex in the series, with a pK_a value of less than 7.0. The relatively high acidity of this complex is attributed to the π-accepting ability of the carbonyl ligand and the high positive charge on the cation. In comparison, *cis*-[Fe(PNP)(PNHP)(CH$_3$CN)$_2$]$^{3+}$ is less acidic because of the replacement of the electron-withdrawing CO ligand with acetonitrile. The lower net charge on *cis*-[Fe(PNP)(PNHP)(H)(CO)]$^{2+}$ and the strong donor character of the hydride ligand result in an increase in the pK_a value for this complex by about 1 unit in comparison with *cis*-[Fe(PNP)(PNHP)(CH$_3$CN)$_2$]$^{3+}$. This difference is similar to that observed for *trans*-[Fe(PNHP)(dmpm)(CH$_3$CN)$_2$]$^{3+}$ and *trans*-[Fe(PNHP)(dmpm)(CO)(H)]$^{2+}$.[10] The trans iron complexes with analogous coligands are 1.1−1.3 pK_a units more basic than the cis derivatives, and this may be a result of stronger donor properties of the dmpm ligand relative to PNP. These comparisons would suggest a pK_a value of approximately 11.5 for *cis*-[Fe(PNHP)(PNP)(CH$_3$CN)(H)]$^{2+}$. It is interesting to note that the pK_a value of the 16e square-planar nickel complex [Ni(PNHP)(dmpm)]$^{3+}$ (8.7)[9] is similar to that observed for the 18e octahedral complex *cis*-[Fe(PNHP)(PNP)(CH$_3$CN)$_2$]$^{3+}$ (8.3). This indicates that the electron-withdrawing/electron-donating properties of the [Ni(dmpm)]$^{2+}$ fragment are comparable to those of the [Fe(PNP)(CH$_3$CN)$_2$]$^{2+}$ fragment.

Low-Temperature Protonation of [HFe(PNP)$_2$(CH$_3$CN)]$^+$ (3). Although hydrogen evolution was very rapid when **3** was protonated at room temperature, more information regarding the protonated products of **3** could be obtained by NMR monitoring of the reactions of **3** with acids of varying strengths at low temperatures. These investigations provide an interesting comparison with observations reported for the protonation of *trans*-[HFe(dmpm)(PNP)(CH$_3$CN)]$^+$ (**1**) under similar conditions. When excess anisidinium tetrafluoroborate is added to **3** in acetone-*d*$_6$ at −78 °C and the NMR spectrum is recorded at a similar temperature, the four phosphorus multiplets are shifted downfield (see the Experimental Section), and a single broad N−H resonance is observed in the ^{1}H NMR spectrum at 8.08 ppm. This product is tentatively assigned as a complex with one protonated ligand, *cis*-[HFe(CH$_3$CN)(PNHP)(PNP)]$^{2+}$ (**3-H**).

When the same experiment is carried out with an excess of the stronger acid cyanoanilinium tetrafluoroborate, the quantitative formation of a complex with two protonated PNP ligands, *cis*-[HFe(CH$_3$CN)(PNHP)$_2$]$^{3+}$ (**3-2H**), is proposed. For this product, a different set of four multiplets are observed in the ^{31}P NMR spectrum at −75 °C, as shown in Figure 1a and detailed in the Experimental Section. The starting complex is regenerated when excess base is added to the solution. When the same protonation reaction is carried out in acetonitrile-*d*$_3$ at low temperatures, two equally intense NH resonances near 8.25 ppm are resolved at −35 °C (total intensity, 2 H) (Figure 1b), consistent with the expected chemical inequivalence of these protons. Also shown in Figure 1b (on an expanded scale) is the hydride resonance (relative intensity, 1H), a doublet of doublet of triplets at −11.25 ppm that indicates coupling of the hydride to four phosphorus atoms.

These results can be compared with those for the trans derivative **1**. When cyanoanilinium ion is reacted with **1** at −78 °C, resonances for two iron−hydride and two N−H resonances are observed that correspond to the endo and exo isomers of the N-protonated product.[12] For the cis derivative studied here

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[21] A revised value for the pK_a value of anisidinium has recently been reported.[20] The pK_a value of *trans*-[HFe(CH$_3$CN)(dmpm)(PNHP)]$^{2+}$ has been recalculated using this new value and is slightly higher (12.7) than the originally reported pK_a = 12.1.[10]

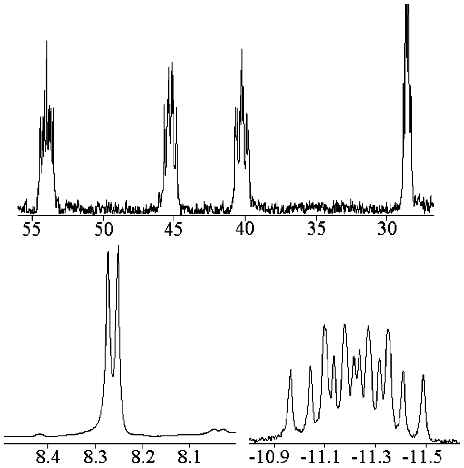
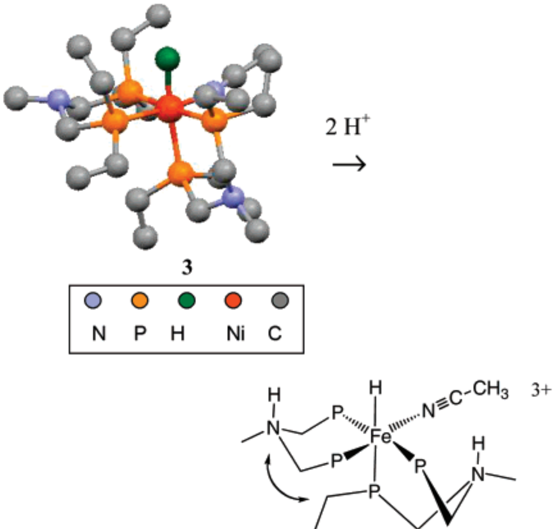


Figure 1. (a, top) ^{31}P NMR spectrum of *cis*-[HFe(CH$_3$CN)-(PNHP)$_2$]$^{3+}$ (**3-2H**), recorded in acetone-*d*$_6$ at −70 °C. (b, bottom) Portions of the 400 MHz ^{1}H NMR spectrum of **3-2H** recorded in CD$_3$CN at −35 °C showing the NH (left) and Fe−H (right) resonances (the relative intensities are not to scale; the hydride resonance has been expanded).

with two PNP ligands, four isomers of the diprotonated complex are possible, but only one isomer is observed. Examination of the molecular structure of the *cis*-[Fe(PNP)$_2$(CH$_3$CN)(CO)]$^{+2}$ cation[10] suggests that the nearly isostructural complex *cis*-[HFe-(CH$_3$CN)(PNHP)$_2$]$^+$, illustrated by structure **3**, would be protonated at positions endo to both the hydride and acetonitrile ligands (reaction 1). As can be seen from structure **3**, protonation in the exo positions, i.e., on the same side as the diethylphosphino group trans to the hydride ligand, leads to significant steric interactions between one ethyl substituent and the axial NH atom. The same argument holds for an NH atom on the second PNHP ligand that is exo with respect to the acetonitrile ligand. Protonation in the endo positions with respect to both the hydride ligand and the acetonitrile ligand should lead to the least sterically hindered and lowest energy structure.



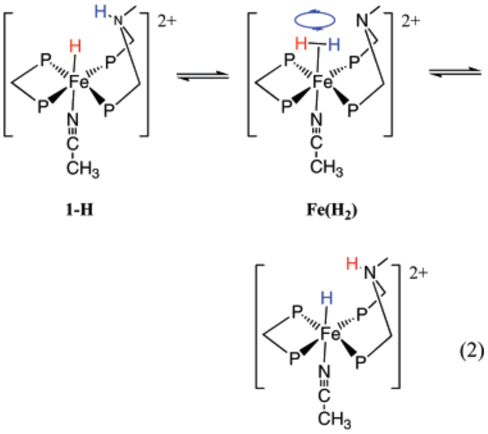
3

3-2H

(1)

In order to probe the potential intramolecular exchange of the Fe−H−H−N sites in **3-2H**, a gradient-enhanced nuclear Overhauser effect spectroscopy (GOESY) NMR experiment was performed using mixing times ranging from 25 to 500 ms over a temperature range of −60 to −25 °C in acetone-*d*$_6$. Inversion of the hydride resonance at −11 ppm did not result in the appearance of an inverted NH resonance, indicating that no exchange is occurring between the metal−hydride and the N−H protons under these conditions. This implies that the rate of exchange must be less than 1 s^{-1} at −25 °C. In contrast, a similar GOESY experiment on the endo isomer of [HFe(CH$_3$-CN)(PNHP)(dmpm)]$^{2+}$ (**1-H**) revealed rapid intramolecular exchange at −60 °C (7.3 s^{-1}), and $\Delta G^{\ddagger} = 11.5$ kcal/mol was determined.[12] The data can be used to calculate an intramolecular exchange rate for **1-H** of 380 s^{-1} at −25 °C, the upper temperature accessible for **2-2H** before H$_2$ loss. Significant differences are therefore observed in the proton relay properties of the PNP ligand in *trans*-[HFe(PNHP)(dmpm)(CH$_3$CN)]$^{2+}$ and *cis*-[HFe(PNHP)$_2$(CH$_3$CN)]$^{3+}$. This difference is attributed to a relatively high energy barrier for the formation of the boat form of the PNHP ligand for the cis complex, and this point is discussed further in the following paragraphs.

The rapid intramolecular exchange in **1-H** was proposed to proceed by reaction 2, in which an intermediate dihydrogen complex is formed. The reaction also suggests a likely intermediate for hydrogen evolution from protonated **1**. In the low-temperature protonation of **1** with triflic acid, a broad resonance was observed in the ^{1}H NMR spectrum at −17 ppm that was assigned to an N-protonated form of the proposed intermediate dihydrogen complex and confirmed by deuterium labeling experiments.[12] In contrast, when **3** was reacted with a strong acid such as triflic acid in acetone-*d*$_6$ at −78 °C, no dihydrogen complex was detected in the ^{1}H NMR spectrum, and the ^{31}P NMR spectrum showed the quantitative formation of *cis*-[Fe-(PNHP)$_2$(CH$_3$CN)$_2$]$^{4+}$, even when the spectrum was recorded only a few minutes after the acid addition. When HBF$_4$ was used under similar conditions, evidence was observed for formation of both *cis*-[HFe(PNHP)$_2$(CH$_3$CN)$_2$]$^{3+}$ and *cis*-[Fe-(PNHP)$_2$(CH$_3$CN)$_2$]$^{4+}$, but no protonation at the iron−hydride site to form a dihydrogen complex, an expected intermediate in the hydrogen evolution reaction, could be detected.



1-H

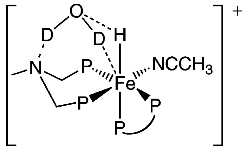
Fe(H$_2$)

1-H

(2)

The relatively slow rate of intramolecular N−H−H−Fe exchange for **3-2H** relative to that for **1-H** seems likely to be a result of unfavorable steric interactions in the cis derivative. In order for either of the cis or trans complexes to undergo the exchange reaction, one PNP ligand must convert from the more stable chair form to the boat conformation. Molecular mechanics calculations have provided insight into this process for both the trans and cis derivatives. The relative energy barrier to form the boat conformer from the more stable chair conformer in a single PNP ligand is 26 kcal/mol for *cis*-[HFe(PNP)$_2$(CH$_3$CN)]$^+$ (**3**) versus only 9.5 kcal/mol for *trans*-[HFe(CH$_3$CN)(dmpm)-(PNP)]$^+$ (**1**) (Figure 3S; Supporting Information). In the trans derivative there is little steric hindrance to this process. However, in **3** both molecular models and the calculations show that steric interactions between ethyl substituents on the cis PNP ligands make the interconversion between chair and boat conformers difficult.

Intermolecular H/D Exchange Reactions. Despite the fact that the intramolecular exchange in **3-2H** is much slower than that in **1-H**, additional experiments suggest that significant intermolecular iron−hydride exchange still occurs with water in solutions of *cis*-$[HFe(PNP)_2(CH_3CN)]^+$ (**3**), and it is enhanced by the presence of the pendant base. Complex **3** was reacted with a large excess (125 equiv) of D_2O in acetonitrile at room temperature, and the disappearance of the iron−hydride resonance was monitored by ^1H NMR spectroscopy. A first-order kinetic plot of the data (Figure 2S; Supporting Information) indicates that the exchange reaction proceeds with a half-life of approximately 1 min. The ^{31}P NMR spectrum confirmed that the complex remains intact in the presence of D_2O. The H/D exchange reaction may proceed by protonation of a pendant amine followed by the intramolecular exchange mechanism shown in reaction 2. Alternatively, a species such as **6**, involving a water molecule associated with the pendant amine base via hydrogen bonding, could mediate the exchange by undergoing concerted formation of Fe−D and O−H bonds. The H/D exchange rate for an octahedral iron derivative in which the diphosphine ligands do not incorporate a pendant base was found to be much slower: e.g., 60% deuterium incorporation after 2.2 h for *trans*-$[HFe(CH_3CN)(depp)(dmpm)](BPh_4)$ (where depp = bis(diethylphosphino)propane).[12] The H/D exchange reactions of the hydride derivatives **4** and **5** with D_2O (125 equiv) in acetonitrile solution were also monitored by NMR spectroscopy, and the pseudo-first-order plots are shown in Figure 2S. For **5**, the half-life for the exchange was approximately 30 min, but no exchange was observed for the hydride ligand in **4** over a period of several days. A similar lack of exchange was reported previously for *trans*-$[HFe(PNP)(dmpm)CO]BPh_4$.[10] The π-acceptor carbonyl ligand in these derivatives makes the hydride ligand relatively acidic. This would make the hydride less susceptible to the interaction with the amine proton proposed in reaction 2 or could disrupt the balance of bond making/bond breaking in the alternate concerted mechanism.



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Summary and Conclusions

The octahedral complex *cis*-$[Fe(PNP)_2(CH_3CN)_2]^{2+}$ (**2**) serves as a useful starting material for the synthesis of a series of substituted derivatives, including *cis*-$[Fe(PNP)_2(CO)(CH_3CN)]^{2+}$ and the new hydrides *cis*-$[HFe(PNP)_2(L)]^+$, where L = CH_3CN (**3**), CO (**4**), $P(OEt)_3$ (**5**). The pK_a values for the first protonated PNP ligand in several of the complexes have been determined in acetonitrile, and values are found to range from <7.0 to 12.7. The differences in acidity of the protonated PNHP ligand in these complexes can be understood in terms of the relative electron-donating and electron-withdrawing abilities of the coligands and the overall charge on the metal complexes. The observation that the pK_a values of the protonated PNHP ligand vary by more than 5 pK_a units as the iron fragment varies indicates that there is considerable electronic communication between the nitrogen atom and the metal center. The acidity of the PNHP ligand depends significantly on the electronic properties of the Fe center to which it is bound.

Steric interactions for the *cis*-$[HFe(PNP)_2(L)]^+$ derivatives investigated in this study appear to play a much more important role than was observed for the *trans*-$[HFe(PNP)(dmpm)(L)]^+$ complexes studied previously in our laboratories. The *cis*-$[HFe(PNP)_2(L)]^+$ complexes incorporating acetonitrile have been found to undergo relatively rapid exchange of this ligand with half-lives ranging from <5 min to 20 min, whereas the rates for the analogous trans complexes are 2 orders of magnitude slower. This difference in reactivity has been attributed to steric interactions between an ethyl group of the PNP ligand and the coordinated acetonitrile ligand for the cis complexes that are not observed for the trans complexes. This difference in steric interactions is also believed to account for the difference in the rates of H_2 loss between the cis and trans complexes. The rate of H_2 loss upon protonation of *trans*-$[HFe(PNP)(dmpm)(CH_3CN)]^+$ was relatively slow (hours required for complete loss of H_2 at room temperature). However, *cis*-$[HFe(PNP)_2(CH_3CN)]^+$ (**3**) undergoes very facile H_2 elimination (ca. 1 min required for complete loss of H_2 at room temperature).

Similarly, significant differences were observed in the proton relay properties of the cis and trans derivatives. The pendant base in the PNP ligand of *trans*-$[HFe(PNP)(dmpm)(CH_3CN)]^+$ (**1**) was an effective proton relay and, upon protonation, very rapid intramolecular NH−HFe exchange was observed with $k = 380\ s^{-1}$ at −25 °C. However, the intramolecular exchange between the iron−hydride and the proton on nitrogen for *cis*-$[HFe(PNHP)_2(CH_3CN)]^{3+}$ is significantly slower than that observed for *trans*-$[HFe(PNHP)(dmpm)(CH_3CN)]^{2+}$, with $k < 1\ s^{-1}$ at −25 °C. The slow intramolecular exchange for *cis*-$[HFe(PNHP)_2(CH_3CN)]^{3+}$ is attributed to unfavorable steric interactions between the ethyl substituents of the cis PNP ligands as one of the chelate rings rearranges from the favored chair conformation to the boat form required for NH−FeH interactions. Although a similar conformational change is required for the PNP ligand in *trans*-$[HFe(PNHP)(dmpm)(CH_3CN)]^{2+}$, this motion occurs without significant steric hindrance. These studies point to the more general observation that the stereochemistry of an octahedral complex is likely to play an important role in controlling the rate of hydrogen exchange and the proton relay properties of PNP and related ligands with an amine base incorporated into the chelate ring.

Experimental Section

General Methods and Materials. All reactions were performed under an argon atmosphere using standard Schlenk line techniques. Solvents were dried using standard procedures and distilled under nitrogen. Deuterated NMR solvents were dried over molecular sieves and degassed using the freeze−pump−thaw method. Sodium tetraphenylborate, hydrogen gas, carbon monoxide, triethyl phosphite, *p*-bromoaniline, anisidine, 2,4-dichloroaniline, 4-cyanoaniline, triflic acid, and fluoroboric acid (48% aqueous solution) were obtained from commercial sources and used without further purification. Aniline and triethylamine were obtained from commercial sources and further purified by distillation over CaH_2. $[Fe(CH_3CN)_6](BF_4)_2$,[22,23] bis((diethylphosphino)methyl)methylamine (PNP),[9] and $[Fe(CH_3CN)_2(PNP)_2](BF_4)_2$ (**2**)[10] were prepared according to literature methods.

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[22] Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1960**, 3705−3711.

[23] Heintz, P. A.; Smith, J. A.; Szalay, P. S.; Weisgerber, K. R. *Inorg. Synth.* **2002**, *33*, 77.

^{1}H NMR and ^{31}P NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. ^{31}P spectra were proton-decoupled and referenced to a phosphoric acid external standard. ^{1}H chemical shifts were referenced to residual solvent proton shifts. VT NMR experiments were allowed to equilibrate for 5 min at each temperature. Information on the GOESY NMR method used in this work is given in the Supporting Information.[24] Electrospray ionization (ESI) mass spectra were collected using an HP 5989B mass spectrometer with an HP 59987A electrospray apparatus. Infrared spectroscopy was performed on a ThermoNicolet Avatar 360 FT-IR ESP spectrometer using potassium bromide pellets. Details of the pK_a calculations are given in the Supporting Information.

Calculations of conformer energy profiles on *cis*-$[Fe(PNP)_2(H)(CH_3CN)]^+$ and *trans*-$[Fe(PNP)(dmpm)(H)(CH_3CN)]^+$ were carried out on the Merck molecular force field (mmff) level with Spartan '04 by Wavefunction Inc. The respective models were built in the program, and the Fe−P−C−N or Fe−P−P−N dihedral angle was systematically varied to create an energy profile of the chair to boat conformational change of the PNP ligand. For the complex *cis*-$[Fe(PNP)_2(H)(CH_3CN)]^+$ the dihedral angle of only one of the PNP ligands was fixed, with the second ligand allowed to assume its lowest energy conformer.

Syntheses. $[HFe(PNP)_2(CH_3CN)](BPh_4)$ (3). Hydrogen was bubbled into a solution of $[Fe(PNP)_2(CH_3CN)_2](BF_4)_2$ (0.354 g, 0.453 mmol), sodium tetraphenylborate (0.883 g, 2.58 mmol), and triethylamine (0.073 g, 0.526 mmol) in acetone (30 mL) for 20 min. The reaction flask was closed, and the solution was stirred overnight. The volume of the solution was reduced to 10 mL, and methanol (20 mL) was added. When the solution was reduced in volume to 10 mL and cooled in a −78 °C freezer, a bright yellow powder was formed, which was filtered and washed with cold methanol. Yield: 0.233 g, 58%. Anal. Calcd for $C_{48}H_{78}BFeN_3P_4\cdot MeOH$: C, 64.00; H, 8.99; N, 4.57. Found: C, 64.15; H, 8.98; N, 4.34. ^{31}P NMR (CD_3CN, ppm): δ_Z 21.4 (ddd); δ_X 36.7 (ddd), δ_M 41.5 (ddd), and δ_A 45.6 (ddd); $^2J_{AM} = 47.4$ Hz; $^2J_{AX} = 76.4$; $^2J_{AZ} = 23.5$; $^2J_{MX} = 54.6$; $^2J_{MZ} = 41.5$; $^2J_{XZ} = 24.7$. ^{1}H NMR (CD_3CN, ppm): 7.32 (m), 7.01 (m), 6.86 (m) (20 H total, BC_6H_5); 3.34−2.89 (m) (8 H total, PCH_2N); 2.39 (s), 2.33 (s) (3 H each, NCH_3); 1.96 (s) (3 H, $NCCH_3$); 1.78 (m), 1.69 (m), 1.45 (m), 1.55−1.32 (m) (16 H total, PCH_2CH_3); 1.17 (m), 1.07 (m), 0.96 (m) (24 H total, PCH_2CH_3); −11.11 (ddt) (1 H, *H*Fe, $J_1 = 31.9$ Hz, $J_2 = 49.9$ Hz, $J_3 = J_4 = 61.3$ Hz). ESI$^+$ (CH_3CN, *m/z*): 527 $\{Fe(PNP)_2(H)\}^+$. IR (KBr, cm^{-1}): ν_{CN} 2252 and $\nu_{FeH} = 1824$. CV ($E_{1/2}$ (ΔE_p) or E_p if irreversible, V vs ferrocene/ferrocenium): oxidations, −0.27 (irr), 0.46 (irr); reductions, −2.33 (irr), −2.75 (irr).

Alternatively, bis(triphenylphosphine)iminium borohydride (0.141 g, 0.256 mmol) was added to a solution of $[Fe(PNP)_2(CH_3CN)_2](BF_4)_2$ (0.181 g, 0.231 mmol) and sodium tetraphenylborate (0.482 g, 1.41 mmol) in acetonitrile. The reaction mixture was then stirred overnight and filtered. All solvent was removed from the filtrate with a vacuum. After the resulting solid was redissolved in a minimum amount of acetone, the complex was worked up in the same manner as described above. Yield: 0.090 g, 44%.

$[Fe(PNP)_2(CH_3CN)(CO)](BPh_4)_2$. The procedure was slightly modified from that previously reported.[10] Carbon monoxide was bubbled into a solution of $[Fe(PNP)_2(CH_3CN)_2](BF_4)_2$ (0.225 g, 0.287 mmol) and sodium tetraphenylborate (1.07 g, 3.12 mmol) in acetone (30 mL) for 20 min. The reaction flask was closed, and then the solution was stirred overnight. The volume of the solution was reduced to 15 mL by applying a vacuum, and then methanol was layered on top. A solid was formed upon cooling to −15 °C overnight. Recrystallization from acetone/ether produced yellow crystals. Yield: 0.231 g, 65%. NMR data have been reported previously.[10] CV ($E_{1/2}$ (ΔE_p) or E_p if irreversible, V): oxidations, −0.27 (irr), 0.51 (irr). reductions, −1.49 (76), −2.30 (irr).

$[Fe(PNP)_2(CO)(H)](BPh_4)$ (4). Carbon monoxide was bubbled into a solution of $[Fe(PNP)_2(CH_3CN)(H)](BPh_4)$ (0.158 g, 0.178 mmol) in acetone (20 mL) for 15 min. The reaction flask was sealed, and the solution was stirred overnight. The volume of the solution was reduced to 5 mL by applying a vacuum, and 20 mL of methanol was stirred in. When the solution was reduced in volume to 10 mL and cooled to −78 °C, a pale yellow solid formed, which was collected by filtration and washed with cold methanol. Crystals were obtained from a solution of acetone/ether. Yield: 0.081 g, 52%. Anal. Calcd for $C_{47}H_{75}BFeN_2P_4O$: C, 64.54; H, 8.64; N, 3.20. Found: C, 64.64; H, 8.90; N, 3.20. ^{31}P NMR (CD_3CN, ppm, *J* in Hz): δ_A 35.3 (ddd), δ_M 32.8 (ddd), δ_X 20.6 (ddd), and δ_Z 16.8 (ddd); $^2J_{AM} = 33.6$; $^2J_{AX} = 78.9$; $^2J_{AZ} = 26.9$; $^2J_{MX} = 50.7$; $^2J_{MZ} = 44.9$; $^2J_{XZ} = 34.8$. ^{1}H NMR (CD_3CN, ppm): 7.32 (m), 7.01 (m), 6.86 (m) (20 H total, BC_6H_5); 3.19 (m), 3.08 (m), 2.43 (m) (8 H total, PCH_2N); 2.40 (s), 2.39 (s) (3 H each, NCH_3); 2.10 (m), 1.99 (m), 1.31 (m), 1.68 (m) (16 H total, PCH_2CH_3); 1.22 (m), 1.09 (m) (24 H total, PCH_2CH_3); −12.68 (ddt) (1 H, *H*Fe, $J_1 = 31.0$ Hz, $J_2 = 48.6$ Hz, $J_3 = J_4 = 60.6$ Hz). ESI$^+$ (CH_3CN, *m/z*): 555 $\{Fe(PNP)_2(H)(CO)\}^+$. IR (KBr, cm^{-1}): ν_{CO} 1931, ν_{FeH} 1898. CV ($E_{1/2}$ (ΔE_p) or E_p if irreversible, V vs ferrocene/ferrocenium): oxidations, −0.71 (irr), 0.48 (irr); reductions, −2.25 (irr); −2.79 (irr).

Alternatively, hydrogen gas was bubbled into a solution of $[Fe(PNP)_2(CH_3CN)(CO)](BPh_4)_2$ (0.135 g, 0.109 mmol) in acetone (10 mL) for 15 min. The solution was sealed and stirred for 10 days. It was worked up in a manner similar to that described above. Yield: 0.033 g, 35%.

$[Fe(PNP)_2(P(OEt)_3)(H)](BPh_4)$ (5). A slight excess of triethyl phosphite (0.033 g, 0.196 mmol) was added to a solution of $[Fe(PNP)_2(CH_3CN)(H)](BPh_4)$ (0.158 g, 0.178 mmol) in acetone (20 mL). The reaction flask was allowed to stir overnight yielding a pale yellow solution. The volume of the solution was reduced to 5 mL by applying a vacuum, and 20 mL of methanol was stirred in. When the solution was reduced in volume to ca. 5 mL and placed in a −78 °C freezer for 1 h, a yellow solid formed that was collected by filtration. The product was recrystallized from acetone/methanol. Yield: 0.097 g, 54%. ^{31}P NMR (CD_3CN, ppm): 19.9 (ddt); 29.1 (br); 36.6 (ddt); 38.5 (br); 166.7 (br). ^{1}H NMR (CD_3CN, ppm): 7.31 (m), 7.02 (m), 6.87 (m) (20 H total, BC_6H_5); 4.07 (q) (6H, OCH_2CH_3); 2.93−2.70 (m), 2.61−2.46 (m) (8 H total, PCH_2N); 2.37 (s), 2.35 (s) (3 H each, NCH_3); 2.08 (m), 1.93 (m), 1.84 (m), 1.63 (m), 1.48 (m) (16 H total, PCH_2CH_3); 1.28 (t) (9 H, OCH_2CH_3); 1.08 (m) (24 H, PCH_2CH_3); −14.48 (ddddd) (1H, *H*Fe, $J_1 = 13.8$ Hz, $J_2 = 37.3$ Hz, $J_3 = 40.4$ Hz, $J_4 = 57.9$ Hz, $J_5 = 82.9$ Hz). ESI+ (CH_3CN, *m/z*): 693 $\{Fe(PNP)_2(H)(P(OEt)_3)\}^+$, 527 *m/z* $\{Fe(PNP)_2(H)\}^+$. IR (KBr, cm^{-1}): ν_{FeH} 1881 (weak). CV ($E_{1/2}$ (ΔE_p) or E_p if irreversible, V vs ferrocene/ferrocenium): oxidations, −0.26 (irr), 0.50 (irr); reductions, −2.41 (irr), −2.56 (irr).

$[Fe(PNHP)_2(CH_3CN)_2](BF_4)_4$ (2-2H). $[Fe(PNP)_2(CH_3CN)_2](BF_4)_2$ (0.069 g, 0.088 mmol) was dissolved in 5 mL of acetone, and HBF_4 (48% in H_2O) (33 μL, 0.26 mmol) was added. After initial stirring for 30 s, the reaction mixture was allowed to sit undisturbed, and over the next several minutes an orange precipitate formed. After approximately 30 min, the precipitate was filtered and dried under vacuum. Yield: 0.067 g, 72%. ^{31}P NMR (CD_3CN, ppm): 30.0 (br); 20.9 (br). ^{1}H NMR (CD_3CN, ppm): 7.63 ppm (s, N*H*). IR (KBr, cm^{-1}): ν_{NH} 2635. Anal. Calcd for $C_{26}H_{62}B_4F_{16}FeN_4P_4\cdot H_2O$: C, 32.00; H, 6.61; N, 5.84. Found: C, 31.37; H, 6.88; N, 5.37 (H_2O was observed in the ^{1}H NMR spectrum of the analyzed sample). CV ($E_{1/2}$ (ΔE_p) or E_p if irreversible, V vs ferrocene/ferrocenium): oxidations, 0.79 (irr), 1.01 (irr); reductions, −1.78 (irr), −2.02 (irr), −2.22 (irr), −2.36 (irr).

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[24] Stott, K.; Keeler, J.; Van, Q. N.; Shaka, A. J. *J. Magn. Reson.* **1997**, *125*, 302−324.

When the reaction was carried out with HOTf or DOTf, the same cation was formed with better solubility in CD_3CN. ^2H NMR (CD_3CN, ppm): 8.34 (s, N*D*). ^{31}P NMR (CD_3CN, ppm): 30.0 (br); 20.9 (br).

Observation of $[Fe(PNHP)(PNP)(CH_3CN)(H)]^{2+}$ (3-H) via NMR. $[Fe(PNP)_2(CH_3CN)(H)](BPh_4)$ (25 mg, 0.028 mmol) and anisidinium tetrafluoroborate (18 mg, 0.085 mmol) were placed in an NMR tube that was cooled in a dry ice/isopropyl alcohol bath, and acetone-d_6 (precooled to −78 °C) was added to the NMR tube. It is important to keep the sample cold; therefore, the NMR tube was only removed from the dry ice bath long enough to transfer it to the precooled instrument. $[Fe(PNHP)(PNP)(CH_3CN)(H)]^{2+}$ was observed in the NMR spectrum at −75 °C. ^{31}P NMR (acetone-d_6, ppm): 45.4 (br); 45.0 (br); 33.9 (br); 28.3 (br). ^1H NMR (acetone-d_6, ppm): −10.42 (br, *H*Fe); 8.08 (br s, N*H*).

Observation of $[Fe(PNHP)_2(CH_3CN)(H)]^{3+}$ (3-2H) via NMR. A process similar to that above was performed, with cyanoanilinium tetrafluoroborate (17 mg, 0.085 mmol) being used instead of anisidinium tetrafluoroborate. ^{31}P NMR (−75 °C, acetone-d_6, ppm): 53.8 (m), 44.7 (m), 39.5 (m), 28.1 (m). ^1H NMR (ppm): 8.48 (s) (2 H, N*H*); −11.09 (ddt) (1 H, *H*Fe, $J_1 = 31.6$ Hz; $J_2 = J_3 = 51.7$ Hz; $J_4 = 66.3$ Hz).

Attempted Observation of $[Fe(PNP)_2(CH_3CN)(H_2)]^{2+}$. Triflic acid (7.5 uL, 0.085 mmol) was placed in an NMR tube containing $[Fe(PNP)_2(CH_3CN)(H)](BPh_4)$ (25 mg, 0.028 mmol) and 0.7 mL of deuterated acetone at −78 °C. The ^{31}P NMR spectrum (−75 °C) taken only 4 min after the addition of triflic acid shows resonances corresponding to the formation of $[Fe(PNHP)_2(CH_3CN)_2]^{4+}$, given above. HBF_4 (11.7 uL, 0.085 mmol) was also used in a similar experiment, but the ^{31}P NMR spectrum at −75 °C showed formation of $[Fe(PNHP)_2(CH_3CN)_2]^{4+}$ and $[Fe(PNHP)_2(CH_3CN)(H)]^{3+}$.

Acetonitrile Exchange. $[Fe(PNP)_2(CH_3CN)(H)](BPh_4)$ (approximately 20 mg) was dissolved in 0.7 mL of acetone-d_6 at 23 ± 2 °C. To this was added 30 μL of CD_3CN (∼25-fold excess) and the normalized integral of the acetonitrile resonance at 2.42 ppm in the proton NMR was followed as a function of time. A first-order plot of this data can be used to obtain a rate of $1.8 \times 10^{-3}\ s^{-1}$, which corresponds to a half-life of 6 min. Using a similar method, half-lives of 34 min ($k = 3.4 \times 10^{-4}\ s^{-1}$) for $[Fe(PNP)_2(CH_3CN)(CO)](BPh_4)_2$ and approximately 1 min ($k \cong 1.1 \times 10^{-2}\ s^{-1}$) for $[Fe(PNP)_2(CH_3CN)_2](BPh_4)_2$ were determined. These experiments were repeated using neat acetonitrile-d_3 by placing approximately 20 mg of complex directly into 0.7 mL of acetonitrile-d_3. This yielded half-lives of <1 min for $[Fe(PNP)_2(CH_3CN)_2](BPh_4)_2$ and 20 min ($k = 5.7 \times 10^{-4}\ s^{-1}$) for $[Fe(PNP)_2(CH_3CN)(CO)](BPh_4)$.

Hydride Exchange with D_2O. $[Fe(PNP)_2(H)(P(OEt)_3)](BPh_4)$ (20 mg, 0.020 mmol) was weighed into a NMR tube and dissolved in CD_3CN. An initial spectrum was taken, and D_2O (50 μL, 2.50 mmol) was added. The integration of the hydride resonance at −14.50 ppm was monitored over time. When the sample was left to stand overnight, the hydride signal completely disappeared. A first-order plot of this data (ln I/I_0 vs time) was used to obtain a rate of $3.9 \times 10^{-4}\ s^{-1}$, which corresponds to a half-life of 30 min. A similar procedure was used to find that $[Fe(PNP)_2(CH_3CN)(H)](BPh_4)$ is 85% exchanged in 4 min. Due to the faster kinetics a rate constant was not obtained, although the half-life is estimated to be in the range of 1−2 min. $[Fe(PNP)_2(CO)(H)](BPh_4)$ did not show any exchange over a period of 2 days.

Attempted Determination of Intramolecular Proton/Hydride Exchange for $[Fe(PNHP)_2(CH_3CN)(H)]^{3+}$ (3-2H). Complex **3-2H** was prepared according to the procedure outlined above. A GOESY experiment was performed in which temperatures were varied from −78 to −25 °C with mixing times ranging from 50 to 300 ms. The magnetization of the hydride peak at −11.09 ppm was selectively inverted, and the resonance of the NH peak at 8.48 ppm was monitored. However, no inverted exchange peak was observed over the entire range of conditions.

pK_a of $[Fe(CH_3CN)_2(PNP)(PNHP)]^{3+}$ (2-H). An excess of triflic acid (11.01 μL, 0.123 mmol) was added to $[Fe(PNP)_2(CH_3CN)_2](BF_4)_2$ (20 mg, 0.025 mmol) in an NMR tube using CD_3CN as solvent. The solution was monitored over 1 h until the ^{31}P NMR shifts of the fully diprotonated species were constant (20.7 ppm, 29.9 ppm). Addition of excess triethylamine shows the reaction to be reversible. $[Fe(PNP)_2(CH_3CN)_2](BF_4)_2$ (20 mg, 0.025 mmol), cyanoanilinium tetrafluoroborate (26 mg, 0.125 mmol), and cyanoaniline (15 mg, 0.125 mmol) were weighed into a NMR tube. This solution was monitored via ^{31}P NMR for 3 h at 23 ± 2 °C to ensure shifts were constant (18.7, 27.6 ppm). This experiment was repeated with a similar 5/5 excess of dichloroanilinium triflate/dichloroaniline, yielding the same shifts. This indicates that the protonation of a single nitrogen is occurring. A 5/5 excess of bromoanilinium triflate/bromoaniline showed only a 0.6 ppm shift. On the basis of these results, the experiment was repeated using 10/2, 21/3, and 14.6/2 ratios of bromoanilinium triflate to bromoaniline. The ^{31}P NMR of $[Fe(PNP)_2(CH_3CN)_2](BF_4)_2$ in CD_3CN shows resonances at 14.5 and 22.0 ppm. Using these values, the shifts for the singly protonated species, and those from the equilibrium shifts, the pK_a can be calculated to be 8.3 ± 0.2. Details of these calculations are given in the Supporting Information.

pK_a of $[Fe(PNP)(PNHP)(CO)(H)]^{2+}$ (4-H). Three equivalents of triflic acid (6.3 μL, 0.071 mmol) was added to $[Fe(PNP)_2(CO)(H)](BPh_4)$ (20 mg, 0.023 mmol) in an NMR tube using CD_3CN as solvent. The solution was monitored over 1 h until the ^{31}P NMR shifts of the fully diprotonated species were constant, which occurred with a color change to pale blue-green (40.2, 35.7, 29.6, 22.6 ppm). Addition of excess triethylamine shows the reaction to be reversible. $[Fe(PNP)_2(CO)(H)](BPh_4)$ (20 mg, 0.023 mmol), cyanoanilinium tetrafluoroborate (47 mg, 0.228 mmol), and cyanoaniline (27 mg, 0.228 mmol) were weighed into a NMR tube. This solution was monitored via ^{31}P NMR for 3 h at 23 ± 2 °C to ensure that the shifts were constant (38.2, 36.6, 27.4, 23.2 ppm). This experiment was repeated using 10/10 dichloranilinium triflate/dichloroaniline (39.1, 36.3, 28.0, 22.8 ppm). The averages of the cyano/dichloro shifts were used as the shifts for the singly protonated complex. Intermediate shifts were observed upon the addition of 10/10 bromoaniline triflate/bromoaniline (36.5, 34.4, 21.9, 20.7 ppm). Determination of the equilibrium constant leads to a pK_a of 9.2 ± 0.3 for the monoprotonated complex.

pK_a of $[Fe(PNP)(PNHP)(CH_3CN)(CO)]^{3+}$. An excess of tetrafluoroboric acid (7.1 mg, 0.081 mmol) was added to $[Fe(PNP)_2(CH_3CN)(CO)](BPh_4)_2$ (20 mg, 0.0162 mmol) in an NMR tube using CD_3CN as solvent. The solution was monitored over 1 h, until the ^{31}P NMR shifts of the fully diprotonated species were constant (10.0, 15.0, 23.3, 23.5 ppm). Addition of excess triethylamine shows the reaction to be reversible. $[Fe(PNP)_2(CH_3CN)(CO)](BPh_4)_2$ (20 mg, 0.0162 mmol), cyanoanilinium tetrafluoroborate (23 mg, 0.113 mmol), and cyanoaniline (13 mg, 0.113 mmol) were weighed into an NMR tube using CD_3CN as solvent. This solution was monitored via ^{31}P NMR for 3 h at 23 ± 2 °C to ensure that the shifts were constant (3.0, 11.7, 17.4, 19.1 ppm). This experiment was repeated a second time with 10/10 cyanoanilinium tetrafluoroborate/cyanoaniline, yielding similar shifts. Only a small shift is seen, which means that the pK_a of $[Fe(PNP)_2(CH_3CN)(CO)](BPh_4)_2$ is <7.2 in acetonitrile.

Attempted Determination of the pK_a of $[Fe(PNP)(PNHP)(CH_3CN)(H)](BPh_4)$ (3-H). Addition of a weak acid such as anisidinium tetrafluoroborate (pK_a = 11.86) results in the immediate release of hydrogen and formation of *cis*-$[Fe(PNP)_2(CH_3CN)_2]^{2+}$. Addition of protonated triethylamine (pK_a = 18.82) results in no reaction.

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Supporting Information Available: Text and figures giving kinetic plots for acetonitrile exchange for **3**−**5** and for deuterium incorporation from D_2O into **3**−**5**, a plot of conformer energies for **1** and **3**, and descriptions of the pK_a calculations and GOESY NMR experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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